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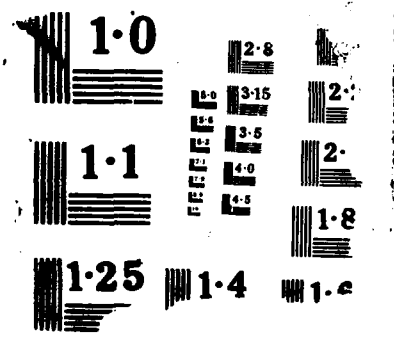
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1a. REPC Uncl		1b. RESTRICTIVE MARKING	
2a. SECURITY CLASSIFICATION AUTHORITY		3. DISTRIBUTION / AVAILABILITY OF REPORT Approved for public release; Distribution unlimited	
2b. DECLASSIFICATION / DOWNGRADING SCHEDULE		5. MONITORING ORGANIZATION REPORT NUMBER(S) AFOSR-TK- 87-1513	
4. PERFORMING ORGANIZATION REPORT NUMBER(S)		7a. NAME OF MONITORING ORGANIZATION AFOSR/NC	
6a. NAME OF PERFORMING ORGANIZATION Department of Chemistry Columbia University	6b. OFFICE SYMBOL (If applicable)	7b. ADDRESS (City, State, and ZIP Code) Bld 410 Bolling AFB, DC 20332-6448	
6c. ADDRESS (City, State, and ZIP Code) New York, NY 10027		9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER AFOSR-84-0013	
8a. NAME OF FUNDING / SPONSORING ORGANIZATION AFOSR	8b. OFFICE SYMBOL (If applicable) NC	10. SOURCE OF FUNDING NUMBERS	
8c. ADDRESS (City, State, and ZIP Code) Bld 410 Bolling AFB, DC 20332-6448		PROGRAM ELEMENT NO. 61102F	TASK NO. 2303
		WORK UNIT B2	WORK UNIT ACCESSION NO.
11. TITLE (Include Security Classification) POLARITY DEPENDENT BARRIERS AND THE PHOTOISOMERIZATION DYNAMICS OF POLAR MOLECULES IN SOLUTION			
12. PERSONAL AUTHOR(S) J.M. Hicks, M.T. Vandersall, E.V. Sitzmann, and K.B. Eisenthal			
13a. TYPE OF REPORT Reprint	13b. TIME COVERED FROM TO	14. DATE OF REPORT (Year, Month, Day)	15. PAGE COUNT
16. SUPPLEMENTARY NOTATION Springer-Verlay (1986)			
17. COSATI CODES		18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)	
FIELD	GROUP	SUB-GROUP	
19. ABSTRACT (Continue on reverse if necessary and identify by block number) To investigate the effects of the solvent on the photoisomerization kinetics of DMABN, we have carried out studies in a series of linear alcohols, alcohol/alkane mixtures, linear nitriles and nitrile/alkane mixtures (part of the data has been reported).			
20. DISTRIBUTION / AVAILABILITY OF ABSTRACT <input checked="" type="checkbox"/> UNCLASSIFIED/UNLIMITED <input type="checkbox"/> SAME AS RPT <input type="checkbox"/> OTHERS		21. ABSTRACT SECURITY CLASSIFICATION Unclassified	
22a. NAME OF RESPONSIBLE INDIVIDUAL Dr. Anthony J. Matuszko		22b. TELEPHONE (Include Area Code) (202) 767-4963	22c. OFFICE SYMBOL NC

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Polarity Dependent Barriers and the Photoisomerization Dynamics of Polar Molecules in Solution

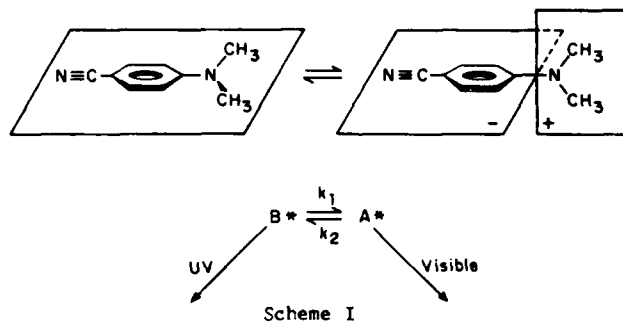
J.M. Hicks, M.T. Vandersall, E.V. Sitzmann, and K.B. Eisenthal

Department of Chemistry, Columbia University, New York, NY 10027, USA

There has been recent theoretical and experimental interest in potential energy barrier descriptions of molecular structural changes in solution [1-7]. For example, the dependence of photoisomerization kinetics on solvent viscosity has been studied to test barrier crossing models [1-5]. Changes in the photoisomerization rates through a solvent series or as a function of temperature have been attributed to viscosity and thermal effects; other possible effects, such as solvent dependent excited state potential surface variations, have generally not been considered [8]. In particular, strong interactions with polar solvents are expected for molecules which undergo a major charge redistribution on isomerization, whether they be polar molecules such as p-dimethylamino-benzonitrile (DMABN) [7], or nonpolar molecules which pass through very polar intermediate structures such as t-stilbene [3-5]. These polar interactions can be important factors in the dynamics of isomerization, as we will show in this paper.

1. DMABN -- Case of a Polar Molecule

DMABN is a classic example of a molecule that exhibits strong solute-solvent interactions, as demonstrated by the fact that its excited state isomerization occurs in polar solvents but not in nonpolar solvents [9]. A general scheme of the dynamics is given in Scheme I [10].



The isomerization takes place on an excited singlet potential surface and involves a 90° rotation of the dimethylamino group about the amino-phenyl bond [10]. This twisting structural change produces an increase in the excited state dipole moment from 6 D to 16 D [11]. In polar solvents, a new visible emission appears due to the solvent stabilized twisted form. Due to a rapid equilibration between the planar (B*) and twisted (A*) structures two emissions are observed. The one in the ultraviolet is due to the planar form and the visible emission is due to the twisted polar form. In alkanes, only the uv emission from B* is observed. Many time-resolved studies have

been conducted on DMABN, yet the role of the solvent is still not clear [7,12-16].

To investigate the effects of the solvent on the photoisomerization kinetics of DMABN, we have carried out studies in a series of linear alcohols, alcohol/alkane mixtures, linear nitriles and nitrile/alkane mixtures (part of the data has been reported [7,12]). A single pulse from the output of a Nd³⁺/glass laser was frequency quadrupled to 265 nm and used to excite DMABN. The fluorescence from the B* and A* states was time-resolved with a streak camera detection system which had a resolution of 7 ps [13].

An important aspect of the solute/solvent interactions is the effect of solvent viscosity on the kinetics of a reaction. From studies in neat liquids, we find a viscosity dependence in nitriles of $\eta^{-2/3}$ and in alcohols, η^{-1} . These can be interpreted as cases of intermediate and strong solute-solvent coupling, respectively. Of key importance in obtaining these viscosity dependences of k_1 is the assumption that only the viscosity differences among the various members of the solvent series affect the rate. The possibility that the potential surface may change in different solvents is not considered, nor are the possibilities that boundary conditions, entropy or dynamic polarity effects vary with solvent. For a polar structural transition such as in DMABN the invariance of the potential cannot be assumed. Specifically, the changes in solvent polarity, even within a polar series, can be of sufficient magnitude to produce marked changes in the excited state barrier height. It has long been recognized that there are barrier height changes in going from a nonpolar to a polar solvent. The issue here is that these barrier effects can come into play within a solvent family, e.g. the polar alcohol series, or in one solvent at different temperatures.

To separate the effects of solvent polarity and viscosity, we have used two techniques: (i) k_1 was measured at room temperature in isoviscous mixtures of a polar solvent and an alkane, where the polarity of the mixture was controlled by the concentration of the polar solvent, and (ii) the temperature was varied for the neat solvents so that the solutions had the same viscosity but different polarity values. In Fig. 1 we see that the isomerization rate is not a constant at a fixed viscosity and temperature, but indeed varies exponentially with solvent polarity as measured by the widely used [17] empirical solvent polarity parameter $E_T(30)$. The fitting of the

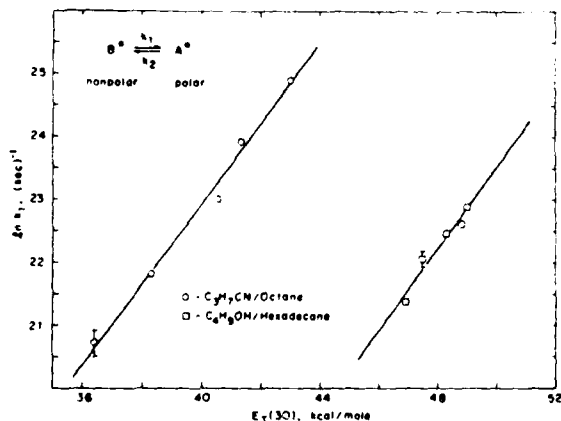


Fig. 1: Plot of $\ln k_1$ for DMABN vs. the solvent polarity parameter $E_T(30)$

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Further support for the effects of solvent polarity on the isomerization dynamics is obtained from our second technique where the same viscosity is obtained by adjusting the temperatures of the neat liquids. The different rates measured have previously been assumed to be due to the different Boltzmann factors. This can be seen in the following Arrhenius-type expression (1): $k = A f(\eta) \exp(-E/RT)$, where E is the barrier height, $f(\eta)$ is the viscosity function (which is a constant for the isoviscosity experiment) and A is the pre-exponential frequency factor. We carried out these measurements in both the neat alcohols and neat nitriles, and found that the rate increases as the temperature is lowered in both solvent families. This result of a "negative" activation energy is contrary to what would be the case if only the Boltzmann factor is changing. To explain these results, we propose that the barrier height is not independent of temperature, but decreases due to a higher solvent polarity at lower temperatures. The polar twisted form of DMABN (A^*) is stabilized relative to the initially excited planar form (B^*), which thereby leads to a smaller barrier. This decrease in the barrier overcomes the usual Boltzmann effect and is responsible for the increased rate at lower temperature. When we correct for the temperature induced polarity changes, we find that the corrected rate decreases as the temperature is lowered, i. e. a normal positive activation energy is obtained, as seen in Fig. 2.

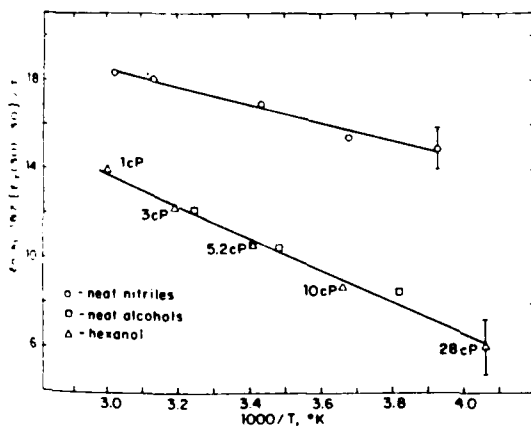


Fig. 2: Arrhenius plot of polarity-corrected rate for DMABN in neat isoviscous nitriles (1.0 cP), neat isoviscous alcohols (5.2 cP), and hexanol at the indicated viscosities

Both the alcohol and nitrile data shown in Figs. 1 and 2 can be explained by introducing a polarity dependent barrier E_a : $E_a = E_a^0 - A [E_T(30) - 30]$, where E_a^0 is the activation energy in an alkane solvent having an $E_T(30)$ of 30 and A is an experimentally determined factor which determines how strongly the barrier height changes with solvent polarity. The corrected rate, r , plotted in Fig. 2, is $k_1 \times \exp -A[E_T(30) - 30]/RT = C \exp(-E_a^0/RT)$, where C is the Arrhenius pre-exponential factor. The values of E_a^0 are found to be 8.0 kcal/mole in the nitriles and 14.0 kcal/mole in the alcohols. Comparing the nitriles and alcohols at a given solvent polarity, we see that the barrier E_a^0 is higher in alcohols by about 6 kcal/mole. We attribute this to the effects of hydrogen bonding between the dimethylamino group of DMABN and the alcohol hydroxy group. The hydrogen bond withdraws electrons

from the electron donating dimethylamino part of DMABN and thereby opposes the electron transfer to the benzonitrile part of DMABN. For the intramolecular charge transfer in DMABN to occur, the hydrogen bond must be broken. This increases the barrier for the isomerization in alcohols relative to nitriles by 6 kcal/mole, roughly the energy of typical hydrogen bonds.

2. *t*-Stilbene -- Case of a Polar Intermediate Structure

The photoisomerization of *t*-stilbene has been studied by many groups to gain insight into how the solvent affects this simple chemical change [3-5]. The observed rate has been discussed in terms of (1), where $f(\eta)$ is either the Kramers function (which gives poor agreement with the observed rates) or more often $\eta^{-\alpha}$. This latter form can be obtained from a free volume [19] or frequency dependent friction model [20-21]. This general equation predicts that at constant viscosity, a plot of $\ln k$ versus T^{-1} should have the slope $-E_a/R$. We have tested this prediction by studying the rates of photoisomerization of stilbene in alcohols at various temperatures under constant viscosity conditions.

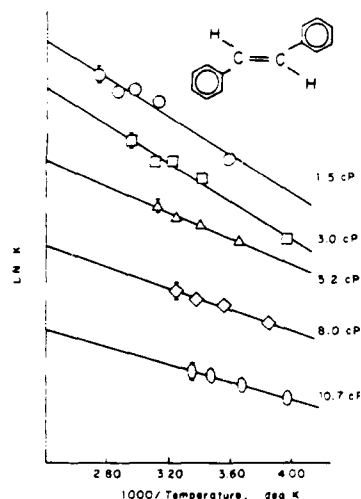


Fig. 3: Plot of $\ln k$ vs. T^{-1} for *t*-stilbene in isoviscous alcohols; the ordinate axis is offset for each viscosity line for viewing purposes

In Fig. 3 it is shown that the slopes of these lines depend on viscosity, contrary to what the equation predicts. The apparent E_a 's vary from 2.6 to 1.2 kcal/mole. A similar deviation from (1) is shown by the dependence of the rate on viscosity at different fixed temperatures. We find that the value of α varies by a factor of two over a 50°K temperature range. This result conflicts with the constant α value predicted by the $\eta^{-\alpha}$ dependence of the rate equation.

Since the isomerization involves an intermediate structure that is highly polar, we ask whether polarity dependent barrier effects are important in the isomerization process. Accordingly, we carried out measurements in neat alcohols at various solvent polarities and temperatures, analogous to our DMABN study. We found that static polarity effects alone do not explain our stilbene results in alcohols. In stilbene, dynamic polarity effects could be important since extensive solvent rearrangements are required in the isomerization from the initial nonpolar form to the twisted charge separated

form. This is not an increase in dipole moment, but a more polar (16 Debye) dipole in the initial solvent molecule. If the solvent is more polar, the isomerization time, dielectric relaxation time, separating the transition state positions of the solvent, and the rate of change of the solvent polarity resolve the role of solvent in the isomerization [30].

Conclusions

We find that the isomerization of DMABN with alcohols is a charge redistribution process. The polarity of the solvent affects the rate of isomerization. The forms of the molecule change from a nonpolar to a polar form within a series of nitriles, and the effect is crucial to the observed rate of DMABN with alcohols. In alcohols, we have found that the frequently applied equation for the rate of isomerization of *t*-stilbene in alcohols, which assumes a static polarity correction, is not valid. Although the *t*-stilbene intermediate structure is static, the dynamic polarity correction is important. The nonpolar initial *t*-stilbene structure is

Acknowledgements: This work was supported by the Air Force Office of Scientific Research, Program 29-85-K-0049

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Structure

studied by many groups to gain chemical change [3-5]. The where $f(\eta)$ is either the observed rates) or from a free volume [19] is general equation k versus T^{-1} should have by studying the rates of various temperatures under

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form. This is not expected for DMABN because its transition involves an increase in dipole moment along the same axis from a polar (6 Debye) to a more polar (16 Debye) form. The solvent is already arranged about the large dipole in the initially excited DMABN, unlike the case for stilbene, where the initial solvent arrangement is that appropriate to a nonpolar solute molecule. If the solvent motions are not very rapid compared to the isomerization time, then the isomerization dynamics would depend on the dielectric relaxation properties of the solvent [22-29]. The energy separating the trans and intermediate form would therefore depend upon the positions of the surrounding solvent molecules, and thus be dependent on the rate of change of the solvent arrangement. Further work is underway to resolve the role of polarity and other solvent factors in the stilbene isomerization [30].

Conclusions

We find that the isomerization dynamics of molecules that involve a large charge redistribution, such as in DMABN, are strongly dependent on the polarity of the solvent. The solute/solvent interaction can be described in terms of a polarity dependent barrier that separates the two structural forms of the molecule. In addition to the well-recognized effects in going from a nonpolar to a polar solvent, we find that the effects of polarity change within a series of related polar liquids, e.g. linear alcohols or nitriles, and the effects of the change in polarity with temperature are crucial to the observed kinetics. We have also found that hydrogen bonding of DMABN with alcohols impedes the isomerization relative to that of nonhydrogen bonding polar solvents such as nitriles. For t-stilbene in alcohols, we have found from measurements at various viscosities and temperatures that the isomerization cannot be described in terms of frequently applied equations which contain an $\eta^{-\alpha}$ power dependence. Although the t-stilbene isomerization passes through a very polar intermediate structure, we are not able to adequately fit the data using a static polarity correction as we did for DMABN. The possibility of a dynamic polarity effect due to a large solvent rearrangement in going from the nonpolar initially excited t-stilbene to the polar twisted intermediate stilbene structure is discussed.

Acknowledgements: The authors wish to thank the National Science Foundation, the Airforce Office of Scientific Research and the Joint Services Electronics Program 29-85-K-0049 for their support of this work.

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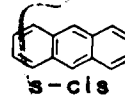
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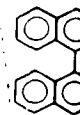
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